PB85-157048

Dynamics of Pollutant Photoreactions in the Hydrosphere

(U.S.) Environmental Research Lab.
Athens, GA

1984

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1. REPORT NO.	2.	3. PB85-157048
EPA/600/J-84/196		

4. TITLE AND SUBTITLE	5. REPORT DATE
Dynamics of Pollutant Photoreactions in the Hydrosphere (Journal Version)	1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
R.G. Zepp, P.F. Schlotzhauer, M.S. Simmons, G.L. Baughman, and N.L. Wolfe	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency Athens GA 30613	AARB1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens GA 30613	Journal article
	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES
Published in Fresenius Z. Anal. Chem. 319(2):119-125, 1984.
Contact: R.G. Zepp, 8-250-3428

16. ABSTRACT

Procedures have been developed for predicting direct photolysis rates of chemicals at low concentrations in air-saturated distilled water. Recently, attention has turned to the more complex problem of quantitating the effects of substances indigenous to aquatic environments on photolysis rates and products. These natural substances influence photolysis rates of pollutants in aquatic environments through initiation of indirect photoprocesses, through attenuation of sunlight, and through physical or chemical interactions that alter the speciation or microenvironment of pollutants. Recent research on these various effects is reviewed, with emphasis on studies of the influence of humic substances, suspended sediments, algae and natural inorganic species on photoreactions of trace organic chemicals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	10
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

EPA/600/J-84/196
JOURNAL ARTICLE

Dynamics of Pollutant Photoreactions in the Hydrosphere

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Dynamik der Photoreaktionen von Verunreinigungen in der Hydrosphäre

Zusammenfassung. Um kinetische Daten über den Einfluß von Sonnenlicht auf das Verhalten von Verunreinigungen in Seen und Flüssen zu erhalten, wurden licht-induzierte Umwandlungsreaktionen von organischen Chemikalien untersucht. Es ergab sich, daß die Humuskomponente der in natürlichen Wässern gelösten organischen Substanzen auf zwei Arten die aquatischen Photoreaktionen beeinflußt. durch Schwächung des Sonnenlichtes und durch Sensibilisierung der Photoreaktionen. Humus-sensibilisierte Photoreaktionen von Furanen, Sulfiden, Dienen, nitroaromatischen Verbindungen u.a. werden diskutiert. Ein Überblick wird gegeben über die Wirkung aquatischer Partikel auf die Geschwindigkeit der Photoreaktion von Verunreinigungen. Suspendierte Sedimente wirken hauptsächlich durch Lichtabschwächung und Streuung auf die Photolysegeschwindigkeit. Algen, Diatomeen und Bakterien beschleunigen lichtinduzierte Umwandlungen von Anilinen und Phosphorthioat-Insecticiden, was darauf hindeutet, daß photobiologische Prozesse eine bedeutende Rolle beim Abbau gewisser Verunreinigungen in aquatischer Umgebung spielen könnten. Es wird gezeigt, daß Nitrat, Eisenverbindungen und Peroxide für die Sonnenlicht-induzierte Oxidation freier Radikale von Verunreinigungen in natürlichen Wässern verantwortlich sein können.

Summary. Light-induced transformations of organic chemicals have been studied to provide kinetic results concerning the influence of sunlight on pollutant behavior in lakes and rivers. A review of these studies shows that the humus component of the dissolved organic matter in natural water affects aquatic photoreactions in two important ways: by attenuating sunlight and by sensitizing photoreactions. Studies of humus-sensitized photoreactions of furans, sulfides, dienes, nitroaromatic compounds, and other chemicals are discussed. Research concerning effects of aquatic particulates on pollutant photoreaction rates are reviewed. Suspended sediments mainly affect photolysis rates through light attenuation and scattering. Algae, diatoms, and bacteria accelerate light-induced transformations of anilines and phosphorothioate insecticides, suggesting that photobiological processes may play a significant role in the breakdown of certain pollutants in aquatic environments. Evidence is presented that nitrate, iron species, and peroxides may be responsible for sunlight-initiated free radical oxidations of pollutants in some natural waters.

Offprint requests to: R. G. Zepp

Concern over the possible adverse effects of man-made chemicals that enter the environment has prompted research efforts on predicting the behavior of such chemicals in the hydrosphere. This paper reviews some of the recent research on sunlight-induced photoreactions of organic pollutants in natural waters, with emphasis on the dynamics of these processes. Results of these studies are being used in computer models that integrate rate and equilibrium data to provide estimates of the exposure concentrations of pollutants in various environmental compartments [1]. The emphasis here is on pollutant photoreactions in freshwater systems, but the results and principles discussed also may apply to light-induced reactions of chemicals in cloud droplets which are now the focus of research by many atmospheric scientists [2], as well as to photoreactions of natural chemicals in the sea [3, 4].

Photochemical transformations occur upon direct absorption of light by a reactive chemical or, alternatively, through indirect processes that involve light absorption by another substance that is in the system with the reactive chemical. The photolysis rate of a chemical in a water body equals the sum of the rates of its various competing direct and indirect photoreactions. As shown in Table 1, both direct and indirect photoreactions in water can be very rapid with full exposure to sunlight.

Procedures have been developed for predicting direct photolysis rates of chemicals at low concentrations in air-saturated distilled water [5, 6]. Recently, attention was turned to the more complex problem of quantitating the effects of substances indigenous to aquatic environments on photolysis rates and products. These natural substances influence photolysis rates of pollutants in aquatic environments through attenuation of sunlight, through initiation of indirect photoprocesses, and through physical or chemical interactions that alter the speciation or microenvironment of pollutants. Recent research on these various effects is discussed here, with emphasis on studies of the influence of humic substances, suspended sediments, algae and natural inorganic species on photoreactions of trace organic chemicals. More detailed reviews of hydrospheric photochemistry appear elsewhere [3, 4, 7, 8].

Table 1. Kinetic parameters of several photoreactive chemicals in sunlight

Compound	Midday k_p^o, h^{-1}	Substrate lifetime, min	Reference
Direct photoreactions			
4-Nitro-1,2-xylene	16	4	20
Triflurallin	2.0	30	5
N-Nitrosoatrazine	8.6	7	41
Hexachlorocyclopentadiene	24	2	25
Pentachlorophenol	2.1	28	42
3,3′-Dichlorobenzidine	23	3	43
Anthracene	0.92	65	44
Pyrene	1.0	60	44
Naphthacene	23	3	44
Ferrocyanide complex	2.1	28	45
Indirect photoreactions			
Trinitrotoluene/Holston river	4.3	14	19
TNT/Scarsville pond	2.1	28	19
Dimethylfuran/Aucilla river	8.3	7	11, 12
2,6-Dinitrotoluene/Aucilla river	3.6	17	20
o-Nitrotoluene/Aucilla river	0.92	65	20

Influence of Humic Substances on Photoreaction

Several studies have demonstrated that photolysis rates of certain organic chemicals are enhanced in the presence of humic substances [9–16]. In some cases, chemicals that are unreactive in distilled water were found to photoreact rapidly in solutions of humic substances or in natural water samples [7]. Usually, when photolysis rates were enhanced by humic substances, different photoproducts also were formed [9–11]. The studies have indicated that humic substances are capable of photosensitizing several types of organic photoreactions. A scheme that summarizes the various reaction pathways is shown in Eqs. (1–7), where S represents the part(s) of humic substances that acts as a sensitizer.

$$S \xrightarrow{\text{Light}} {}^1S^* \longrightarrow {}^3S^* \tag{1}$$

$${}^3S^* \xrightarrow{k_d} S \tag{2}$$

$${}^3S^* + O_2 \xrightarrow{k_{ox}} S + {}^1O_2 \tag{3}$$

$${}^3S^* + Q \xrightarrow{k_q} S \tag{4}$$

$${}^3S^* + RH \xrightarrow{k_I} I \begin{cases} \rightarrow \text{Products} \\ \rightarrow RH \end{cases} \tag{5}$$

$$I = \begin{cases} S + {}^3RH \\ SH\cdot + R\cdot \\ S^{-}\cdot + R^{+}\cdot \\ S^{+}\cdot + R^{-}\cdot \end{cases}$$

$${}^1O_2^* \xrightarrow{1/\tau_0} O_2 \tag{6}$$

$${}^1O_2^* + A \xrightarrow{k_A} AO_2. \tag{7}$$

Light absorption promotes a photosensitizer molecule to its first excited singlet state ${}^1S^*$ [Eq. (1)]. Singlet excited states, with lifetimes only on the order of 10 ns or less, are far too short lived to significantly interact with organic pollutants, RH, at the very low concentrations that occur in aquatic environments. Molecules in singlet states, however, decay in part by undergoing intersystem crossing to excited triplet states, ${}^3S^*$, which are considerably longer lived. A variety of pathways may deactivate such triplets [Eqs. (2–5)]. These include decay to ground state [Eq. (2)], energy transfer to molecular oxygen [Eq. (3)], or some other interaction that quenches ${}^3S^*$ [Eq. (4)], and various interactions with pollutants in the natural water [Eq. (5)]. Interactions with pollutants could possibly include electronic energy transfer to form triplet states of substrate, ${}^3RH^*$, hydrogen atom transfer, and oxidation or reduction processes. Intermediates formed from these pollutant-sensitizer interactions can go on to become products and/or in some cases can revert to unaltered substrate.

Singlet oxygen ${}^1O_2$, the product of energy transfer to molecular oxygen [Eq. (3)], is an excited form of oxygen that is a more powerful oxidant than ordinary oxygen. It reacts rapidly with certain "acceptors", A' [Eq. (7)] often forming peroxidic products. Reactions of singlet oxygen with various substrates referred to as "oxygenations", must compete with its decay back to ordinary oxygen [Eq. (6)].

In addition to the various processes depicted in Eqs. (1–7), peroxides derived from humus photoreactions or trace metals complexed by substances may photoinitiate free radical oxidations of various substrates [Eqs. (8–9)].

$$R - X \xrightarrow{\text{Light}} R + X \tag{8}$$

$$R(X) + RH\,(+\,O_2) \rightarrow \text{Products}. \tag{9}$$

At pollutant concentrations that are very low, the above reactions can be described by rate expressions that are first order with respect to pollutant concentration [RH]; that is, the rate equals k_s [RH] where k_s is the rate constant, which is expressed in units of reciprocal time.

Oxygenations photosensitized by humic substances have been studied in detail [11–14, 16]. Zepp and co-workers [11, 12] have reported oxygenations of furans and sulfides in sunlight (Fig. 1). The oxygenation of 2,5-dimethylfuran (DMF) was studied to obtain detailed information about photosensitization by humic substances. The DMF studies were conducted at sufficiently low concentrations to insure that the reaction was not complicated by the competing free radical reactions that can be initiated by the peroxidic products [14]. Several mechanistic tests established that the oxidation of DMF in natural water samples was mediated by singlet oxygen [11]. For example, the oxygenation of DMF in a swamp water containing dissolved humic substances was affected by DABCO (1,4-diazabicyclo [2.2.2] octane) and deuterium oxide in the same way as the photooxygenation of DMF sensitized by rose bengal, a known singlet oxygen sensitizer [11]. Other studies involving DMF as a substrate indicated that rates of sunlight-induced oxygenations sensitized by the humic substances in a river water were independent of hydrogen-ion activity from pH 5 to pH 10 [12].

Because humic substances are known to be mixtures of refractory chemicals derived mainly from plant decay, it was assumed [11, 12] that humic substances from different

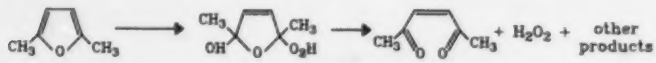

Fig. 1
Photosensitized oxygenations that occur in natural waters

Table 2. Kinetic data for oxygenation reactions photosensitized by humic substances in water exposed to sunlight [12]

Humic source	Relative rate constant[a, b, c]	
	2,5-Dimethylfuran[d]	Disulfoton[e]
Distilled water	< 0.01	< 0.1
Aucilla river, FL	1.0	1.0
Okefenokee swamp, GA	1.13 ± 0.32 (4)	–
Quincy bog, NH	1.52 ± 0.08 (4)	–
Williamson river, OR	1.22 ± 0.40 (4)	–
Fulvic acid, CA[f]	1.52 ± 0.40 (3)	1.2 ± 0.0 (3)
Contech fulvic acid[f, g]	0.98 (1)	1.1 ± 0.1 (2)
Aldrich humic acid[f, g]	1.21 ± 0.17 (6)	1.1 ± 0.4 (3)
Karl Roth humic acid[f, g]	0.50 ± 0.25 (4)	–
Fluka humic acid[f, g]		
Lot A	0.81 (1)	1.2 ± 0.4 (2)
Lot B	0.68 (1)	1.15 ± 0.4 (2)
Lot C	0.80 ± 0.14 (9)	1.30 ± 0.53 (5)
Lot D	0.80 ± 0.15 (4)	1.2 (1)

[a] Ratio of the sunlight photolysis rate constant to that observed for the photooxidation in Aucilla river water
[b] All solutions optically matched by adjusting absorbance to 0.20 (1.00 cm cell) at 366 nM
[c] Number of experiments in parentheses; each experiment involved triplicate kinetic runs for each solution
[d] Half-life in Aucilla river water ranged from about 20 min in winter to 5 to 10 min during summer at midday
[e] Half-life ranged from about 5 h of midday sunlight during summer to 12 h during winter
[f] Isolated from soils
[g] Obtained commercially

locations would exhibit very different photochemical behavior. Results of several studies, however, indicated that just the opposite is the case. Detailed studies with sunlight of monochromatic light indicate that humic substances in a wide variety of water bodies or humic and fulvic acids extracted from soils have very similar photosensitizing capacities [12, 13]. These similarities are illustrated by comparisons of kinetic data obtained for photosensitized oxygenations of DMF and the insecticide disulfoton in sunlight (Table 2) [12]. Similar findings have been reported for other types of photoreactions that are sensitized by humic substances [9, 12] including a *cis-trans* isomerization that involves electronic energy transfer from sensitizer to 1,3-pentadiene and reactions involving hydrogen transfer from aniline to sensitizer (Fig. 2). The reaction shown for aniline also occurs with the herbicide metabolite 3,4-dichloroaniline in competition with its direct photoreaction [9].

To more quantitatively determine the effects of varying reaction conditions on the photosensitizing efficiencies of

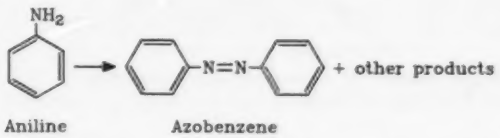

Fig. 2. Photosensitized reactions in natural waters that involve electronic energy transfer (pentadiene reaction) and hydrogen atom transfer (aniline reaction) [12]

various humic substances, response functions, $X_{s,\lambda}$, have been determined for the photosensitized oxygenation of DMF employing monochromatic light. Response functions were computed using Eq. (10):

$$X_{s,\lambda} = \frac{k_{s,\lambda}}{E_o^{av}(\lambda)} \tag{10}$$

where $k_{s,\lambda}$ is the observed first order rate constant for the oxygenation and $E_o^{av}(\lambda)$ is the average irradiance in the reaction cell at wavelength λ. It can be shown that Eq. (11) relates the X_2 for a singlet oxygen reaction to the quantum yield for singlet oxygen production, Y_s, and the absorption coefficient (Napierian) of the solution, a_λ

$$X_{s,\lambda} = k_A\, \tau_o\, a_\lambda\, Y_s. \tag{11}$$

In Eq. (11), k_A is the rate constant for reaction between the acceptor, e.g. DMF, and $^1O_2$ and τ_o is the lifetime of singlet oxygen in water. As predicted by theory [13], experimental results indicated that X_s for the DMF reaction is directly proportional to the concentration of humic substance. Kinetics studies at various wavelengths indicated that response functions for photooxygenation of DMF sensitized by humic substances in the Aucilla River and by soil-derived humic acids were the same within a factor of 2 in the near ultraviolet (UV) and visible spectral regions (Fig. 3). The humic substances in the river water were much more effective in the middle UV, however. The wavelength dependence for the reaction (300 – 500 nm) in Aucilla River water can be described by Eq. (12) where X_{s,τ_o} is the response function at wavelength λ_o and λ is in nanometers:

$$X_{s,\lambda} = X_{s,\lambda_o}\, e^{0.023(\lambda_o - \lambda)}. \tag{12}$$

The response function decreases more rapidly with increasing wavelength than does the absorption coefficient for

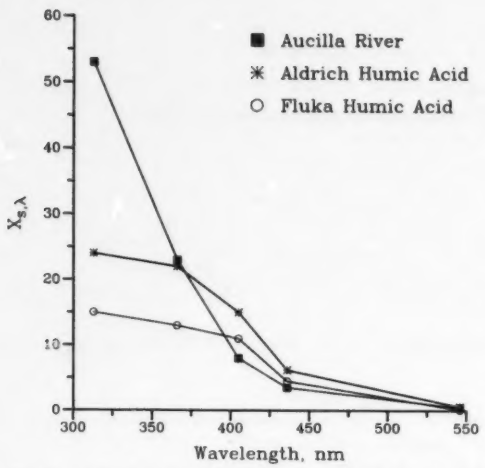

Fig. 3. Action spectra for photosensitized oxygenation of 2,5-dimethylfuran in optically-matched solutions of humic substances [13]

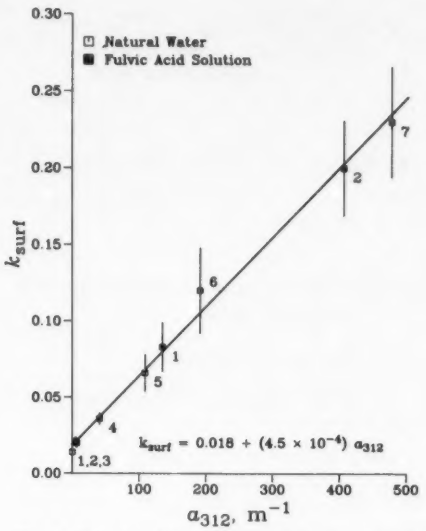

Fig. 4. Relationship between rate constants for photoreaction of 2,4,5-trichlorophenoxyacetic acid and absorption coefficients of various natural water samples from US surface waters [17]

the river water, indicating that the quantum yield for singlet oxygen production decreases with increasing wavelength. Results from an earlier study indicated that Y_s at 366 nm for several natural water samples averaged about 4.3% [11].

Employing computer-generated values for near-surface solar spectral irradiance $E_o(\lambda O)$ [5], rate constants were computed for the photosensitized oxygenation of DMF in sunlight using Eq. (13) [13]:

$$k_{s,\lambda} = E_o(\lambda,O)\ X_{s,\lambda}. \qquad (13)$$

The computations indicate that solar UV light is most effective at promoting reactions sensitized by humic substances in the river water whereas blue light is most effective in the case of the humic acids. The computer also was used to integrate $k_{s,\lambda}$ over all wavelengths to obtain sunlight rate constants k_s. The computed values indicated that near surface half-lives for the DMF reaction should be 5 to 10 min at midday during summer at latitude 40° N. These findings were in close agreement with experimental values (Table 2).

Kinetics studies in sunlight have been employed to estimate steady-state concentrations of singlet oxygen, $[^1O_2]$. Under constant illumination $[^1O_2]$ equals k_s/k_A. Estimates of $[^1O_2]$ computed by Zepp and co-workers [11] and Zafiriou [4] range from about 10^{-14} M to 10^{-12} M. The $[^1O_2]$ approximately correlated with the near UV absorption coefficients (366 nm) of the freshwater and marine water samples indicating that humic substances probably sensitized the $^1O_2$ formation. Because the spectral curves for dissolved substances in freshwater and coastal marine waters are usually very similar in the UV region, the observed correlation is likely to be observed at other UV wavelengths as well.

Correlations between rate constants for sensitized photoreactions in natural waters and UV absorption coefficients also have been found for reactions that do not involve singlet oxygen. For example, Skurlatov and co-workers [17] have found an excellent correlation between the rate constants for photosensitized reaction of the herbicide 2,4,5-T in sunlight and the UV absorption coefficients of natural waters and fulvic acid solutions (Fig. 4). Likewise, Zika and Cooper [18] have reported a similar finding in the case of hydrogen peroxide formation in natural waters exposed to sunlight.

In addition to the studies described above, other studies by Mill and co-workers [15] have indicated that alkoxy, alkylperoxy, and hydroxyl radicals are formed upon exposure of natural waters to sunlight. Such radicals may be derived from photolysis of peroxides that form as products of reactions between singlet oxygen and substances in the water. Mill and co-workers [15] used cumene (CUH) and pyridine (C_5H_5N) as probes to determine steady-state concentrations of the radicals $[RO_2^{\bullet}]$ and $[HO^{\bullet}]$, in sunlight-exposed natural water samples.

An interesting effect of humic substances on photolysis rates of 2,4,6-trinitrotoluene (TNT) was recently reported by Mabey and co-workers [19]. The rate constant for this photoreaction is enhanced up to 100-fold with humic substances present. These authors have suggested that the enhancement is caused by triplet energy transfer. Simmons and Zepp [20], however, have found that triplet sensitization by humus cannot account for the large enhancements, which occur mainly with *o*-alkyl substituted nitroaromatics. The enhancement may be attributable to catalysis of direct photolysis of the nitroaromatics, possibly via chemical trapping by humus of reactive intermediates that revert to starting material in distilled water.

Effects of Suspended Sediments on Photoreactions

Hydrophobic pollutants in aquatic environments are known to partition to the clay and silt-sized particles collectively referred to as "suspended sediments." Several recent studies have examined the photoreactivity of nonpolar organic chemicals in aqueous suspensions of natural sediments [21–25].

Oliver and co-workers [22] investigated the possibility that photolysis rates of sorbed or dissolved organic

Table 3. Effects of suspended sediments on the sunlight photolysis rates of hexachlorocyclopentadiene (1.5×10^{-7} M") [25]

Source of sediment	Sediment concentration, mg/l	Sunlight k_p, h^{-1}	Ratio[b]
North Oconee river, Athens, GA	0	19.0 ± 0.7	
	45	19.7 ± 1.5	0.99 ± 0.11
	0	10.9 ± 0.8	
	45	9.5 ± 0.6	0.87 ± 0.12
Mississippi river, McClure, IL	0	19.9 ± 0.7	
	59	18.7 ± 0.7	0.94 ± 0.06
	0	10.9 ± 0.8	
	59	9.9 ± 0.4	0.91 ± 0.10
Ohio river, Ceredo, WV	0	19.9 ± 0.7	
	63	16.8 ± 2.2	0.84 ± 0.14
Missouri river, Stanton, ND	0	3.8 ± 0.5	
	61	5.3 ± 0.3	1.4 ± 0.26
	0	4.4 ± 0.4	
	61	5.1 ± 0.2	1.2 ± 0.17
Ohio river Ripley, OH	0	3.8 ± 0.5	
	63	5.2 ± 0.3	1.4 ± 0.26
	0	4.4 ± 0.4	
	63	4.9 ± 0.2	1.1 ± 0.16

[a] Exposed to sunlight in 13 mm o.d. test tubes (1 cm light pathlength), each rate constant average of three points

[b] Ratio of rate constant in suspension to rate constant in distilled water

chemicals may be enhanced by indirect photoreactions. Aqueous suspensions of several common clay minerals and a semiconductor powder, TiO_2, were exposed to UV radiation in the presence of free radical scavengers that were dissolved in the system. Results indicated that only TiO_2 produced free radicals upon irradiation. Additional studies indicated that TiO_2 photocatalyzed the decomposition of *p*-dichlorobenzene in water through an indirect photoprocess but that various clays and natural sediments were ineffective. Finally, it was shown that photolysis of methoxyclor (300 nm) was slower in the presence of suspended sediments than in distilled water. The slowdown was attributed to light attenuation by the sediments. In their studies of the pollutant, hexachlorocyclopentadiene, Wolfe and coworkers [25], examine the kinetics of its photolysis in suspensions of sediments from various U.S. locations. Results of the studies (Table 3) indicated almost no effect of the sediments on the rate of photolysis in sunlight.

Miller and Zepp [23] compared the photolysis rates and products of four organic chemicals at trace concentrations in suspensions of natural sediments obtained from water bodies of the United States. The kinetic data were analyzed to disentangle the effects of light attenuation and scattering from the influence of sorption upon photoreactivity of the chemicals. The photoreactivities of the DDT metabolite DDE and the phenyl ketone *m*-trifluoromethylpentadecanophenone were found to be different in the sorbed state than in water, increasing with DDE but decreasing with the ketone. Product studies indicated that the sorbed chemicals were in a microenvironment that is a considerably better hydrogen donor than water.

The studies discussed above were conducted after equilibrating the suspensions for short time periods, usually

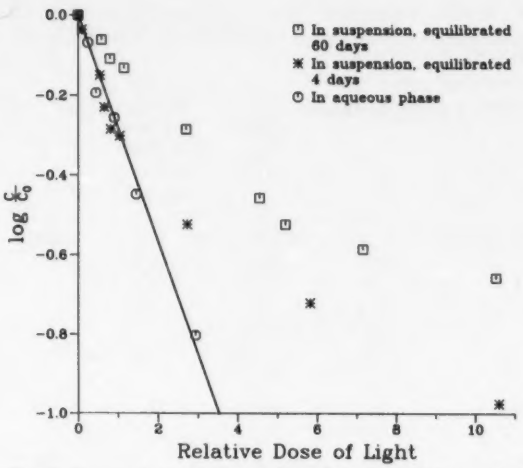

Fig. 5. Comparison of kinetic data for photoreaction of DDE in distilled water and in aqueous suspension of Ohio river sediments [24]

less than one day, prior to irradiation. Pollutants that are resistant to biodegradation or hydrolysis, however, may remain sorbed in soil or bottom sediments for a long time prior to introduction into the water column of water bodies by runoff or resuspension. Zepp and Schlotzhauer [24] have reported that photolysis rates of DDE sorbed in aqueous sediment suspensions are affected by the length of the time that the DDE is sorbed on the sediments (Fig. 5). The terms Co and C in Fig. 5 refer to the initial concentration of DDE in the suspension and the concentration after exposure to light, respectively.

The kinetic data for photolysis of sorbed DDE could be satisfactorily described by the model shown in Eq. (14):

$$\begin{array}{ccccc} P & \underset{k_r}{\overset{X_1 K_p}{\rightleftharpoons}} & R & \underset{k_{-u}}{\overset{k_u}{\rightleftharpoons}} & U \\ k_p \downarrow & & \downarrow & & \\ \text{Products} & & \text{Products} & & \end{array} \qquad (14)$$

This model, which is consistent with Karickhoff's interpretation of sorption kinetics [26], provides that the sorbed DDE, although predominantly photoreactive immediately after sorption, gradually diffuses into a microenvironment where the chemical is unreactive. The symbols *P*, *R*, and *U* represent concentrations of DDE dissolved in the aqueous phase, sorbed on the reactive part, and sorbed on the unreactive part, respectively. When the system is irradiated *P* and *R* rapidly photoreact, and the photolysis becomes rate-limited by diffusion of DDE from the unreactive to the reactive microenvironment. Kinetic parameters derived from analysis of the data indicated that: (1) after 60 days about half of the sorbed DDE was unreactive, (2) the DDE sorbed in the reactive part reacts at a higher rate than when it is dissolved in water, (3) at least 200 h are required for one-half of the DDE sorbed in the unreactive part to diffuse into the reactive part.

One common thread in the above studies was that the predominant effect of sediments on photoreaction of nonionic organic pollutants is a slowing caused by light attenuation. Using photolysis rates of UV-absorbing chemicals as a tool, Miller and Zepp [21] have obtained semi-quantitative data on light attenuation and scattering effects by sediments.

Table 4. Kinetic parameters for transformation of selected organophosphorus compounds in suspensions of *Chlorogonium* sp. exposed to Sunlight [31]

Compound	$(k_p)_p/(k_p)_{act}$ [a]	Chl *a* conc., mg/l	Ratio of algae to distilled H_2O, results	K_{ow} [b]
Methyl parathion	0.58	6.8	10	2,100
	0.53	6.8	8.8	
	0.39	6.3	6.5	
	0.16	1.8	2.7	
	0.10	0.68	1.7	
	0.06	0.0068	1.0	
	0.06 [c]	0	–	
Parathion	1.6	6.8	27	6,500
	0.06	0	–	
Fenitrothion	1.38	1.7	1.0	2,400
	1.33	0	–	
Ronnel	0.66	2.9	22	76,000
	0.03	0		
Chlorpyrifos	< 0.01	2.2	< 2	130,000
	0.04	0		
Diazinon	< 0.1	2.4	–	
	< 0.1	0	–	
Malathion	0.5	7.8	> 25	
	< 0.02	0		
MTB	7.4	8.4	0.8 [d]	
	9.2	0		

[a] Mean of three determinations is reported; standard deviation is typically ± 15% of mean value
[b] Octanol-water partition coefficients
[c] Same value observed in distilled water and supernatant of centrifuged algal suspension.
[d] Assumed to involve light attenuation only

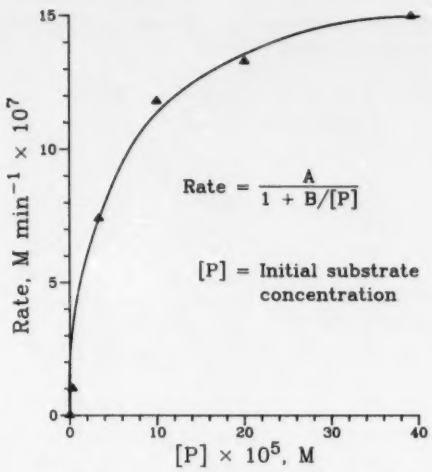

Fig. 6. Rate of light-induced reaction of aniline as a function of initial aniline concentration with Chlamydomonas sp. present [31]

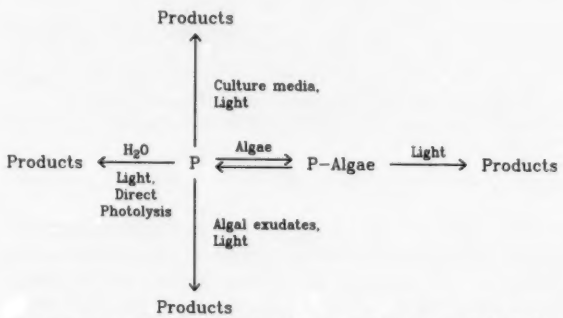

Fig. 7. Proposed mechanism for effects of algae on sunlight-induced transformation of pollutants [31]

Light-Induced Reactions Involving Algae

Algae are known to photometabolize polar, ionic organic substrates such as amino acids, carbohydrates, and carboxylic acids [27]. Non-ionic compounds, including some pollutants, have been shown to photoreact more rapidly with algae present [28 – 30] under laboratory conditions that typically were very dissimilar to outdoor conditions.

Recently, Zepp and Schlotzhauer [31] have provided unequivocal evidence that an assortment of algae can accelerate sunlight-induced reactions of non-ionic organic chemicals in water. Studies of the reactions of organophosphorus compounds (Table 4) indicated that reaction rates are first-order with respect to algae and substrate concentration and that the rate constants are subject to a hydrophobic effect. Kinetic data for reaction of aniline (Fig. 6) at various substrate concentrations could be described by a hyperbolic rate expression. In addition, substances released by the algae were shown to photosensitize the transformation of aniline. Based on these results, Zepp and co-workers have proposed a mechanism for algal-induced photoreactions of pollutants (Fig. 7) involving reversible sorption of substrate by the algal cells. Several other results indicated that the photosynthetic apparatus was not involved in the transformations. For example, the photosynthesis inhibitor DCMU had no effect on the algal-induced photoreactions of methyl parathion and aniline.

Other scientists have presented results indicating that algae release photosensitizing substances when growing in water. Momzikoff and co-workers [32] have reported that the photosensitized oxidation of tryptophan was particularly rapid in aquarium water that had contained various flora and fauna. Likewise, Draper and Crosby [33] and Sinelnikov [34] have found that photochemical production of the oxidant hydrogen peroxide is particularly rapid in highly eutrophic natural waters. The light-induced algal oxidation of naphthalene may involve such an intermediate [35]. Matsumura and Esaac [36] reported very high photosensitizing activity from the chemicals released when algae were heat killed in boiling water and suggested that flavins were probably the photosensitizers. Taken as a whole, these results suggest the intriguing possiblity that there may well be a close relationship between the photosensitizing and biological activity of aquatic systems.

Light-Induced Reactions Involving Natural Inorganic Species

A number of recent studies have provided evidence that various inorganic species in natural waters may have an

important influence on sunlight-induced reactions of trace pollutants in the hydrosphere. Nitrite, nitrate, hydrogen peroxide, and various trace metals are environmental species that may induce indirect phototransformations.

Research concerning the photoreaction of nitrite and nitrate in marine systems has been recently reviewed by Zafiriou [4]. Nitrite photolysis yields NO and hydroxyl radicals. The former is a very stable radical species that has been detected at sea [37], but the latter is highly reactive and may be involved in pollutant transformations. Studies by Kotzias and co-workers [39] have, in fact, shown that the free radicals generated by photolysis of nitrite and nitrate in natural waters are capable of oxidizing various trace organic substrates. Using benzene as a chemical probe for the hydroxyl radical, Russi and co-workers [39] have estimated that the sunlight photolysis of nitrate generated a near-surface steady-state concentration of $5 \times 10-16$ mol/l in a water sample that contained 11 mg/l of nitrate. This [OH·] is more than an order of magnitude greater than that found by Mill and co-workers [15] in several U.S. natural water samples. The difference is possibly attributable to the much higher concentration of radical-scavenging humic substances in the waters studied by Mill. Russi and co-workers [34] estimated that the near-surface halflives for nitrate-induced photoreactions of a great number of aquatic pollutants lie in the range of 80–400 h.

Hydrogen peroxide has been shown to be a constituent of the hydrosphere, both in water bodies [18, 33, 34] as well as in cloud droplets [2]. Draper and Crosby [33] and Zika and Cooper [18] have demonstrated that H_2O_2 forms in various natural-waters exposed to sunlight. Hydrogen peroxide can transform pollutants by various mechanisms. These mechanisms include: (1) direct reactions between H_2O_2 and reactive substrates such as sulfides and phosphines and (2) free radical oxidations involving initial decomposition of H_2O_2 by enzymes, trace metals, and/or light. Draper and Crosby [40] and Skurlatov et al. [17] have found that the sunlight-induced oxidation of pesticides is catalyzed with H_2O_2 present, particularly when trace levels of iron salts are present in the water [17].

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Received January 20, 1984

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